STUDIES ON THE INITIATION OF POLYMERIZATION

I. ELECTROLYTIC REACTIONS
II. DIAZONIUM FLUOBORATES IN ACID

BY

HENRY Z. FRIEDLANDER

A.B., Oberlin College, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

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ACKNOWLEDGMENT

The writer expresses his appreciation for the guidance of Professor Carl S. Marvel, who suggested this investigation, and also wishes to thank Professor Sherlock Swann, Jr., who co-operated in the electro-organic portion of the work.

This research was performed under the auspices of the Synthetic Rubber Division of the Reconstruction Finance Corporation.

R. UNIV. BIBLIOTHEEK LEIDEN

STUDIES ON THE INITIATION OF POLYMERIZATION

I. ELECTROLYTIC REACTIONS

Introduction

The purpose of this research was to determine the feasibility of initiating vinyl polymerization by free radicals formed electrolytically. In this process an ion which can gain or lose an electron at the proper electrode would be transformed momentarily into a free radical, which would preferentially attack the vinyl monomer thereby starting the polymerization reaction. Both ionizible and nonionizable compounds were used as starting material. The problem resolved itself into finding a reaction environment equally suitable for the electrolysis, the transfer of the intermediate to the correct site, and the polymerization.

Previously, vinyl polymerizations have been carried out by electrolysis of the monomer (1,2) and electrolytic regeneration of an initiation activator (3). No one has reported the use of a free radical, formed electrolytically from other than the monomer, as an initiator of polymerization.

Discussion Of Results

A survey was carried out on those electro-organic reactions which were considered most likely to have free radical intermediates. Four cathodic reactions and four anodic reactions were performed in the presence of vinyl monomers. Since the emulsion method leads to the most effective polymerizations and has the lowest energy of activation, most of the experiments were of this type. In addition, some use was made of the solution and suspension methods of polymerization.

The cathodic reactions studied were: the reduction of acetophenone to the pinacol, the electrolysis of methyl iodide, the coupling of quaternary quinolinium salts to dihydrobiquinolyls, and the discharge of *p*-bromobenzenediazonium

ion. The reactions of the following anions were investigated: laurate, *p*-benzyl phenolate, hydroxide, and tricarbethoxymethyl. Whenever possible compounds were chosen which would yield large free radicals preferentially soluble in the monomer phase. Due to electrolytic considerations the various classes of emulsifiers were used, namely, cationic, anionic, neutral ionic, and nonionic. A variety of electrodes, kinds of stirring, methods of deaeration, and current densities were employed.

After over seventy attempts to polymerize several monomers in solution, suspension, and emulsion it was concluded that the free radical intermediates, especially selected for desirable size and reactivity, at both anodes and cathodes do not leave the metal surface. The intermediates did not form addition compounds with the monomers, nor did the latter seem to affect the normal reaction on the electrode.

In the course of this work a new polymerization initiation system was discovered, but this reaction is non-electrolytic in nature. The second part of the thesis deals with the latter method for the initiation of polymerization.

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II. DIAZONIUM FLUOBORATES IN ACID

Introduction

In the previous experiments on the electrolytic generation of free radicals for the initiation of polymerization, hydroquinone was used as a "shortstop." Its addition immediately

after the electrolysis was supposed to preclude polymerization due to aging or the boiling off of an organic extraction solvent. While working-up those runs involving the cathodic discharge of *p*-bromobenzenediazonium fluoborate, it was observed that extensive polymerization of acrylonitrile had occurred after the addition of hydroquinone, but not before. Tests showed that the sulfuric acid anolyte solution and the fluoborate anion were not involved. Further study demonstrated that the diazonium fluoborate-hydroquinone interaction caused the initiation of polymerization. Because this had taken place in acidic solution, there were possibilities for a new acid side emulsion polymerization formula. Since carboxylic, sulfonic, and phosphonic acids and esters are sometimes used as monomers or comonomers, the successful development of new acid polymerization formulas (1) is desirable. Oftentimes new emulsion polymerization procedures of ordinary potency and reaction rate yield polymers, particularly of the rubber type, with different properties due to minor alterations in stucture.

Discussion Of Results

The nature and extent of the initiation of polymerization by diazonium fluoborates in acidic media were studied. A new vinyl polymerization formulation was developed for acid side emulsions and water or dioxane solutions. At 30° the initiation was aided by the use of hydroquinone or Mohr's salt (ferrous ammonium sulfate hexahydrate) as a reducing activator (2), but at 50° the addition of a reducing activation agent gave no better results than without this addition.

The vinyl monomers which could be effectively polymerized were acrylonitrile, styrene, methyl methacrylate, and methyl acrylate. The system was ineffective for vinyl acetate and butadiene. Copolymers of acrylonitrile with butadiene and styrene and of styrene with butadiene were produced.

The highest molecular weight and best conversions to polyacrylonitrile were obtained at a *p*H of 3.0.

The polymers of acrylonitrile formed most readily and had inherent viscosities in the range of four to seven. All the various copolymers had inherent viscosities in the order of 0.2 to 0.6.

The polymerization seems to be of a free radical type, but it proceeds in the presence of hydroquinones, dinitrochlorobenzene, nitrobenzene, and air which are generally considered to be free radical reaction supressors. The only previous use of diazonium fluoborates as polymerization initiators has been in alkaline media.

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VITA

Henry Z. Friedlander was born on May 18, 1925, in New York City and was educated in Scarsdale, New York. In January 1942 he entered Oberlin College. His studies were interrupted by service as a radar technician in the United States Navy. He received the Bachelor of Arts degree from Oberlin in February 1948 and then became a research staff member at the Case Institute of Technology. In the autumn of 1948 he entered the Graduate College of the University of Illinois where he obtained the Master of Science degree in June 1949. While studying at Illinois he first held a University research assistantship and later another from the Synthetic Rubber Division of the Reconstruction Finance Corporation.